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ODOR AND ODOROUS CHEMICAL EMISSIONS FROM ANIMAL BUILDINGS: PART 5 –CORRELATIONS BETWEEN ODOR INTENSITIES AND CHEMICAL CONCENTRATIONS (GC-MS/O)

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ABSTRACT

Simultaneous chemical and sensory analysis based on gas chromatography-mass spectrometry-olfactometry (GC-MS-O) of air samples from livestock operations is a very useful approach for quantification of target odorous gases and also for ranking of odorous compounds. This information can help link specific gases to odor, that can assist in solving farm odor problems and in evaluating of odor mitigation technologies. In this study, we applied the fundamental Weber-Fechner law to correlate the odor intensity and odorous chemical concentration for 15 individual target compounds (from GC-MS-O) for the gas samples collected from four livestock facilities (dairy barns in Wisconsin and Indiana and swine barns in Iowa and Indiana) over a one year period. The results showed that most of the correlations between odor intensities and chemical concentrations for the 15 odorous VOCs sampled fit well with the Weber-Fechner law and had correlation coefficient (R^2) greater than 0.65, with R^2s of 0.84, 0.83, and 0.82 for 4-methylphenol, 3-methylbutanoic acid, and 3-methylindole, respectively. The odorous compounds with higher mean odor activity value (OAV) values fit better with the Weber-Fechner law whereas the odorous compounds with lower mean OAV values resulted in relatively poor R^2 values to the relatively large variations for odor intensities obtained from GC-MS/O for these compounds with low concentrations. The correlations for odorous compounds between odor intensities and chemical concentrations for swine sites were much better than that for dairy sites. R^2s for eight out of fifteen compounds for the two swine sites were greater than 0.60 whereas only one R^2 (butyric acid) was greater than 0.60 for two dairy sites.

KEYWORDS. Animal feeding operation, odor, odor intensity, chemical concentration, volatile fatty acids (VFAs), phenolics, indolics, Weber-Fechner law, correlation, GC-MS/O

INTRODUCTION

Greater concentrations of livestock in confined areas lead to more frequent complaints of odor nuisance by surrounding communities. Odor is induced by the inhalation of volatile odorant compounds. Some authors (Schiffman, et. al., 2005a, and 1998; Wing, et. al., 2008a) have suggested that odors have potential environmental and health effects and there are at least three mechanisms by which odors may produce health symptoms depending on the level of odorants' concentration. At concentrations high enough to stimulate the trigeminal nerve, odorous compounds may produce irritation of the eyes, nose, and throat, or other toxicological effects. At concentrations higher than the olfactory nerve but below the trigeminal nerve threshold, via innate aversion, conditioning, or stress responses, odorous compounds can induce symptoms such as nausea, vomiting, headaches, stress, negative mood, and a stinging sensation. Thirdly, symptoms occurring in response to odorous gas mixtures may be due to a nonodorant component such as endotoxin, which can induce inflammation and airflow obstruction. Evidences of health-

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related effects associated with odor in both laboratory and rural community surveys have been reported (Wing, et. al., 2008a, and 2008b; Schiffman, et. al., 2005b).

Because of growing concerns about livestock odors there is an urgent need to determine odor emissions levels from livestock facilities. Presently, there are two general aproaches used to measure odor, either indirectly by measuring individual gas concentrations in an gas mixture or directly by using a human sensory method such as olfactometry. The US EPA has estabilished several standards for measuring individual gas concentrations in air, such as TO-15 sampling in specially-prepared canisters and TO-17 sampling onto sorbent tubes (US EPA, 1999a, and 1999b). Recently, Trabue et al. (2008) reported a field sampling method for quantifying odorants in humid environments using sorbent tubes and thermal desorption - gas chromatography – mass spectometry (GC-MS). Dynamic forced-choice olfactometry appears to be the most accepted olfactometry method (McFarland, 1995) for quantifying total odor, which relies on air sample collection in bags for subsequent evaluation with panelists. Jacobson et al. (2008) reported standard protocols for sampling and measuring odor emissions from livestock buildings using dynamic forced-choice olfactometry. However, both approaches have strengths and weaknesses. Regulations just based on gas concentrations may reduce specific gas emissions but not adequately address the odors sensed by people downwind from a source (Jacobson, et. al., 2008). Dynamic forced-choice olfactometry does not allow for identification of individual odorous compounds that might be significant to health effects and overall odor control. Developing methods linking the individual gas concentration and odor intensity and character will be much more beneficial for scientists to determine potential health risks associated with agriculture air quality and for governments to enact new air standards that may address odor issues.

Gas chromatography (GC)-mass spectrometry (MS)/olfactometry (GC-MS-O) offers the advantages of combining sensory assessment with the identification and quantification of compounds. This technique is commonly used in the flavor an fragrance industry to identify odorants in complex natural mixtures from plants, fruits and foods (Zellner, et. al., 2008; Plutowska, et. al., 2008). Gallagher et. al. (2008) proved that combined use of GC-MS and GC-O is an effective methodolgy for analyzing the structure of paint volatiles and their sensory properties and holds promise for solving many odorous indoor air problems. Some researchers have reported using this method for identification of odorous compounds from swine facilities (Koziel, et. al. 2006; Bulliner, et. al., 2006; Cai, et. al., 2006; Keener, et. al. 2002; Oehrl, et. al. 2001). Rabaud et. al. (2002) used thermal desorption-GC-olfactometry/MS to identify and quantify odor compounds from a dairy farm. However, relatively few references exist on simultaneous chemical and sensory quantative analysis of livestock odorants (Zahn, et. al., 2001a, and 2001b). Additionally, quantifying odor emissions from animal agriculture is a complex process and few researchers and engineers have taken on the difficult task (Jacobson, et. al., 2008).

This study funded by USDA-NRI supplemented the recently completed National Air Emission Monitoring Study (NAEMS) with comprehensive measurements of odor emissions and chemical analysis of odorous compounds from four NAEMS sites including two swine sites and two dairy sites. This paper is Part 5 in the five-paper series presenting results of this project. Part 1 focuses on project overview and collection methods; Part 2 reports odor emission factors from four NAEMS sites; Part 3 focuses on chemical emission factors; Part 4 addresses correlations between sensory and chemical emissions; Part 5 (this paper) deals with correlations between GC-MS-O and chemical concentrations.

Recently, we have developed a new method for field sampling and simutaneous sensory and chemical analysis of livestock odorant compounds using sorbent tube thermal desorption GC-MS/O (Zhang, et. al., 2010). Fifteen odorous VOCs and semi-VOCs identified from livestock operations were quantified. Odor character, odor intensity and hedonic tone associated with each of the target odorants were also analyzed simultaneously. In this work, we apply the same concept of simultaneous chemical and sensory analyses to gas samples collected from four livestock facilities (dairy barns in WI and IN and swine barns in IA and IN) over a one year period. The objectives of this paper are: 1) to determine the correlations between odor intensities and chemical concentrations of 15 target odorous VOCs; 2) to discuss the differences between correlations associated with compounds, groups of chemicals, odor sources and animal species.

MATERIALS AND METHODS

Sample Collection and Analyses

The detailed experimental section has been illustrated in our previous work (Zhang, et. al., 2010) and Part 1 of this series of papers (Bereznicki, et. al., 2010). Briefly, simultaneously chemical and sensory analyses were performed by using GC-MS/O system sampling with sorbent tubes. Fifteen target odorous VOCs were quantified. In this Part, we used the data collected in the period from February to May, 2009 (i.e. the fourth sampling round), with a total of 12 sampling events and 44 samples (25 from swine site and 15 from dairy site). Hedonic tones of individual compounds were also measured and recorded during sample analysis (data not presented in this work).

Correlation between Odor Intensities and Chemical Concentrations

Correlation and regression analyses were conducted to assess potential correlations between individual chemical concentrations and odor intensities obtained from sniff port on GC-MS/O based on Weber-Fechner law:

$$I = m\log C + b \qquad (1)$$

where I is the odor intensity (category scaling, 0-100), C is the chemical concentration ($\mu g\ m^{-3}$), m is a stimulus-dependent constant that represents the slope of the linear function, b is a stimulus-dependent constant that represents the y axis intercept.. In the Web-Fechner law (Eq. 1), the VOC concentration should not be zero. And for the samples with concentrations below their odor detection thresholds (ODT), the odor intensity should be considered zero and independent with the chemical concentration. So we decided not to use the data with zero values for chemical concentration or odor intensity to do correlation and regression analyses.

Odor Activity Value for Individual Compounds

The odor intensity of individual compound is dependent not only on the chemical concentration, but also on the odor detection threshold value (ODT), the lowest concentration of a certain odorous compound that is perceivable with the human sense of smell. Each individual chemical has different ODT. ODTs are unknown for a small subset of odorous VOCs . Odor activity value (OAV) is a ratio of measured gas concentration to the ODT. The ODT concept was used in the present work to analyze the effects of chemical concentration and ODT on odor intensity. OAV has been used in research related to livestock air quality (Trabue, et. al., 2008). Table 1 lists ODTs cited from Devos' work (1990) and mean OAVs. The mean OAV was estimated using mean measured concentration of the individual compounds divided by their ODTs, respectively.

RESULTS AND DISCUSSION

Correlations between Odor Intensities and Chemical Concentrations

In our previous publication (Zhang, et. al., 2010), based on the simultaneous analyses of livestock odor-causing gases with GC-MS/O, we showed that the correlations between odor intensities and masses of standard gases analyzed followed the fundamental Web-Fechner law. In this study, the same concepts were applied to the gas samples collected from four NAEMS sites instead of standard gases. Table 1 listed the correlations between odor intensities (measured with GC-O) and chemical concentrations. The results indicate that the concentrations of each VOC correlated well with the log odor intensities, i.e. fitting well with the Weber-Fechner law. As seen in Table 1, most of the compounds had R^2 values greater than 0.650, with 4-methylphenol, 3-methylbutanoic acid, and 3-methylindole having R^2s of 0.840, 0.828, and 0.818, respectively.

There are three chemical groups for the 15 target odorous compounds including volatile fatty acids, phenolics, and N-containing odorous compounds (indolics). The average R^2 value for each of the above chemical groups is 0.567, 0.706 and 0.539, respectively. The correlation between R^2s and mean OAVs are shown in Figure 1. As can be seen, higher mean OAVs are corresponding to higher R^2 values. For the samples with lower mean OAV, due to the increase of the variation of the odor intensity obtained from GC-MS/O, it resulted in the relative poor correlation ($R^2 < 0.50$) between odor intensity and concentration.

Table 1 Correlations between measured odor intensities (GC-O) and chemical concentrations for four NAEMS sites (* mean OAV = mean measured concentrations / ODT)

No.	Retention Time	Compounds	ODT ($\mu g\ m^{-3}$)	Mean* OAV	*m*	*b*	R^2
1	12.49	Acetic acid	343	0.363	10.6	2.19	0.728
2	14.07	Propanoic acid	104	0.974	5.91	25.4	0.671
3	14.59	2-Methyl propanoic acid	67.8	0.230	3.17	43.3	0.369
4	15.67	Butyric acid	13.5	7.356	9.50	37.5	0.763
5	16.4	3-Methyl butanoic acid	9.90	1.721	8.80	53.9	0.828
6	17.58	Pentanoic acid	19.3	1.189	5.35	41.6	0.502
7	19.35	Hexanoic acid	57.7	0.181	6.82	42.1	0.401
8	19.81	2-Methoxy phenol	3.70	0.689	7.72	57.2	0.651
9	21.1	Heptanoic acid	142	0.001	5.16	64.1	0.272
10	21.78	Phenol	468	0.016	7.87	36.6	0.540
11	22.93	4-Methylphenol	7.95	4.077	8.07	41.7	0.840
12	24.31	4-Ethyl phenol			6.49	51.2	0.793
13	25.24	1-(2-Aminophenyl)-ethanone			-4.13	20.3	0.064
14	27.92	Indole	0.146	6.199	4.31	54.0	0.734
15	28.62	3-Methylindole	2.91	0.621	3.85	56.4	0.818

*Mean OAV = mean measured concentrations/ODT.

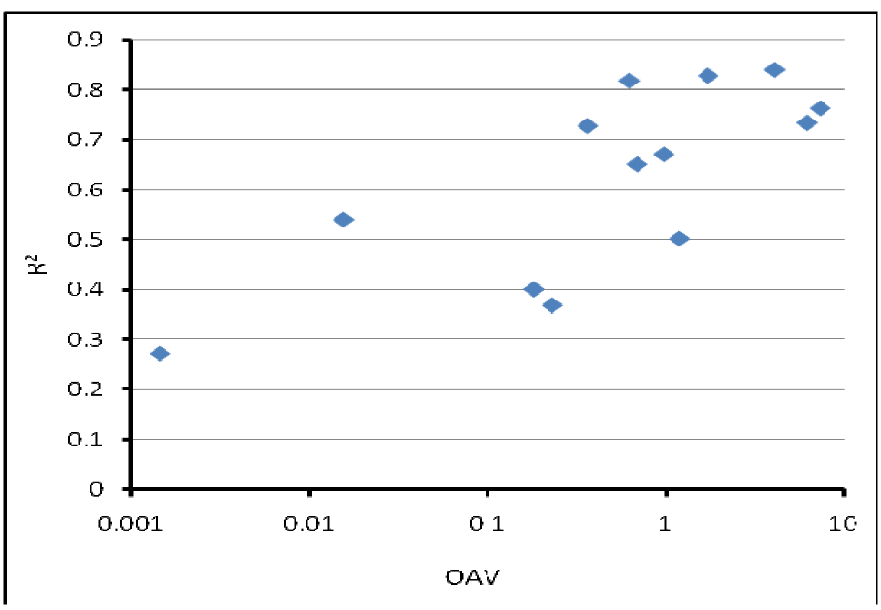

Figure 1 Correlation between OAV and R^2 for the samples from all the sites.

Correlations between Different Odor Sources (Animal Species)

Table 2 summarizes correlations between odor intensities and chemical concentrations separately for the swine and dairy sites. Correlations for swine sites were much better (higher R^2) than for the dairy sites. R^2s for eight out of 15 compounds for swine sites were greater than 0.60 whereas only one R^2 (butyric acid) was greater than 0.600 for dairy sites. Figure 2 shows the correlation between R^2s and mean OAVs for swine sites and dairy sites. The mean OAVs for the odorous compounds from swine sites were much greater than for the dairy sites.

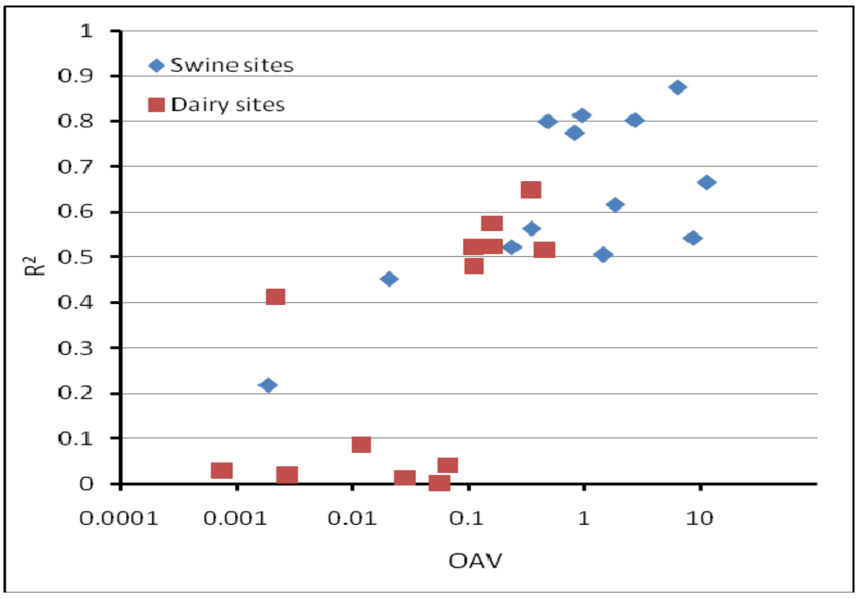

Figure 2 Correlations between OAV and R^2 for the samples from swine and dairy sites separately.

Table 2 Correlations for odorous compounds between odor intensities and chemical concentrations of the samples collected from swine and dairy sites.

No.	Compounds	Swine sites				Dairy sites			
		Mean OAV[a]	*m*	*b*	R^2	Mean OAV[b]	*m*	*b*	R^2
1	Acetic acid	0.487	10.6	1.63	0.800	0.163	12.0	-2.27	0.525
2	Propanoic acid	1.46	5.27	29.1	0.507	0.111	4.43	26.4	0.523
3	2-Methyl propanoic acid	0.353	6.17	34.8	0.564	0.012	1.50	44.6	0.086
4	Butyric acid	11.4	9.85	35.7	0.666	0.347	9.69	38.0	0.65
5	3-Methyl butanoic acid	2.73	10.3	50.2	0.803	0.112	5.78	51.9	0.481
6	Pentanoic acid	1.85	8.39	33.9	0.617	0.057	0.274	39.6	0.001
7	Hexanoic acid	0.238	8.39	39.4	0.523	0.028	-1.54	42.9	0.014
8	2-Methoxy phenol	0.956	10.9	55.7	0.814	0.067	1.37	46.3	0.042
9	Heptanoic acid	0.002	5.13	68.2	0.219	0.0007	0.802	43.4	0.029
10	Phenol	0.021	12.5	26.4	0.453	0.003	0.981	38.8	0.02
11	4-Methylphenol	6.44	8.43	40.3	0.876	0.459	7.21	42.6	0.517
12	4-Ethyl phenol		6.18	52.2	0.722		4.91	47.6	0.473
13	1-(2-Aminophenyl)-ethanone		1.74	56.6	0.025		0.796	44.1	0.012
14	Indole	8.66	4.18	54.0	0.543	0.162	4.86	56.3	0.575
15	3-Methylindole	0.828	4.34	56.2	0.775	0.002	2.41	49.2	0.413

a: Mean OAVs from two swine sites. B: Mean OAVs from two dairy sites. Mean OAV = mean measured concentrations/ODT.

CONCLUSIONS

Simultaneous chemical and sensory analyses for gas samples collected at four NAEMS sites (dairy barns in WI and IN and swine barns in IA and IN) were performed using a GC-MS/O. The following conclusions were drawn from this study:

(1) Linear correlations for measured odor intensities and measured chemical concentrations of most of the 15 target odorous VOCs fit well with the Weber-Fechner law. The highest R^2 values were associated with 4-methylphenol, 3-methylbutanoic acid, and 3-methylindole having R^2s of 0.840, 0.828, and 0.818, respectively.

(2) The odorous compounds with higher mean OAV values also fit better with the Weber-Fechner law whereas the odorous compounds with lower mean OAV values resulted in

relative poor correlations due to the relative large variations in odor intensities obtained from the GC-MS/O.

(3) The correlations between measured odor intensities and chemical concentrations for swine sites were higher than those for dairy sites. R^2s for eight out of fifteen compounds for swine sites were greater than 0.600 whereas only one R^2 (butyric acid) was greater than 0.600 for the dairy sites.

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